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(54) **Dental filling composition and method.**

(57) A root canal sealing dental filling composition, includes liquid polymerizable organic monomers and filler. The polymerizable organic monomers include an diepoxide monomer and a primary monoamine and/or a disecundary amine monomer. The filler includes 40 to 85 percent by weight of the composition and provides a radiopacity of at least 3 mm/mm Al. A method of sealing a tooth canal, includes providing a canal in a tooth sealing the canal with this root canal sealing dental filling composition.

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The invention relates to dental filling composition. A dental filling composition in accordance with the invention is adapted to form epoxide-amine addition polymers with fillers. The dental filling composition include filler and diepoxides, primary monoamines and/or disecndary diamines. Dental filling compositions in accordance with the invention polymerize to form a thermoplastic linear polymer which is adapted to seal a canal in a tooth root. The filler is present in an amount of from 40 to 85 percent by weight of the dental filling composition. The dental filling material is formed by polymerization and has radiopacity of greater than 3 mm/mm Al. The clinical working time is up to about 2 hours and the setting time is from about 0.5 to about 40 hours.

Blahman et al in USSR 311637 and 311638 disclose dental filling materials. Feichtinger et al in U.S. Patent 3,317,469 discloses reaction product of a glycidyl polyether and diaminomethyltricyclodecane. Lee in U.S. Patent 3,327,016 discloses epoxide compositions cured with 1,4-bis(aminomethyl)cyclohexane. Toepel et al in U.S. Patent 3,673,558 discloses polyaddition products and process for their manufacture. Rogier in U.S. Patent 4,229,376 discloses polycyclic polyamines. Rogier in U.S. Patent 4,296,004 discloses polycyclic polyamines. Hörhold et al in U.S. Patent 4,308,085 discloses process for the preparation of high molecular thermoplastic epoxide-amine-polyadducts. Fujisawa et al in U.S. Patent 4,931,096 discloses sealer for filling a dental root canal. Chang et al in U.S. Patent 4,950,697 discloses thermoplastic and injectable endodontic filling compositions. In U.S. Patent 5,236,362 a root canal filling and adhesive composition is described. Polyfunctional aliphatic and aromatic amines such as hexamethylenediamine, diethylene triamine, triethylene tetramine, methylene dianiline or m-phenylenediamine used for the epoxide-amine polymerisation as well as tertiary amine initiators such as 2,4,6-tris(dimethylaminoethyl)phenol or triethanol amine lead to insoluble cross linked network polymers. Cross linked polymers generally tends to higher shrinkage during polymerization which gives rise to the formation of edge cracks and gaps.

Prior art dental filling materials for tooth root canals have relatively long setting time, high viscosity and discolor. Paraformaldehyde is sometimes used, as see Soviet Union Patent 1510131, and Chemical Abstracts 115 (1991) 78952z. Other products contain low molecular weight organic substances like CHI_3 , as see Japanese Patent 9127308 A2, and Chemical Abstract 115 (1991) 78973g. Aliphatic and cycloaliphatic epoxides have been applied in dental filling materials hardened with imidazoline or BF_3 as see Soviet Union Patents 549150, 545353, 52106 and 349396, but are known to have mutagenic properties. Other dental filling materials contain epoxides, diethylenediamine and fillers like porcelain powder, quartz and zeolite, as see Soviet Union Patents 311638 and 311637. These fillers do not provide substantial radiopacity. The use of a setting aliphatic amine alone is disadvantageous because it does not withstand tensions caused by shrinkage and change of temperature. Aliphatic amines cause side reactions (etherification of hydroxyl groups) in epoxide-amine addition polymerization. Consequently a portion of amine groups are unreacted.

High molecular weight linear epoxide-amine addition polymers (M_n 10000 to 20000 g/mol) have been synthesised using diglycidyl ethers of bisphenols and N,N'-dibenzyl diamines, as see DD 141667, US 4308085, GB 2045269, CS 227363; or primary monoamines as see DD 154945, DD 214381, DD 261365. The addition polymers were prepared as adhesives for optical and electrophotographic application.

It is an object of the invention to provide a dental filling material which provides a radiopacity of at least 3 mm/mm Al.

It is an object of the invention to provide a tooth root filling composition which has a radiopacity of at least 3 mm/mm Al and a viscosity less than 20,000 cp.

BRIEF DESCRIPTION OF THE INVENTION

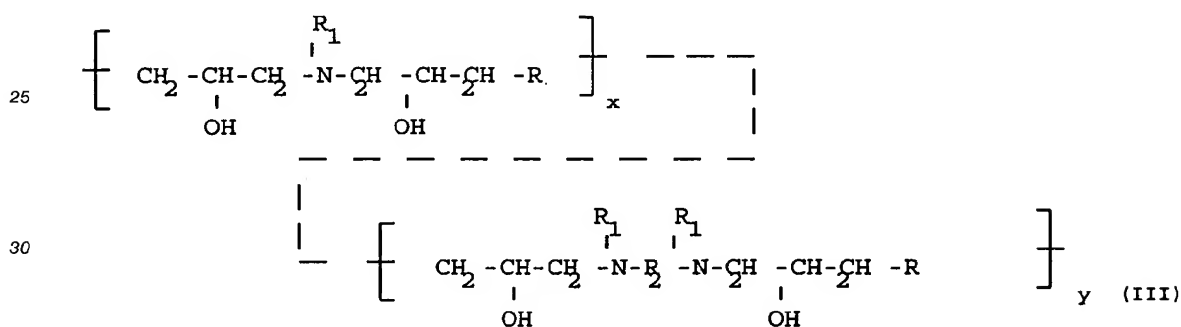
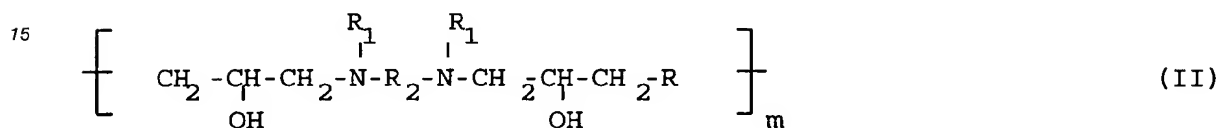
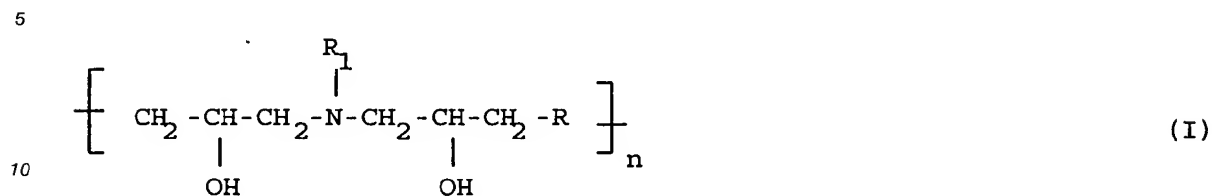
A root canal sealing dental filling composition, includes liquid polymerizable organic monomers and filler. The polymerizable organic monomers include a diepoxide and a primary monoamine and/or a disecndary diamine. The filler includes 40 to 85 percent by weight of the composition and provides a radiopacity of at least 3 mm/mm Al. A method of sealing a tooth canal, includes providing a canal in a tooth sealing the canal with this root canal sealing dental filling composition.

DETAILED DESCRIPTION OF THE INVENTION

Dental filling material in accordance with the invention includes liquid polymerizable organic monomers and fillers, and is adapted for sealing tooth root canal such as are formed by root canal procedures. The polymerizable organic monomers are diepoxides, primary monoamines and/or disecndary diamines. Unsubstituted aliphatic primary monoamines, which form with diepoxide, crosslinked polymer, are not preferred as polymerizable organic monomers in dental filling material in accordance with the invention. Filler content in dental filling material in accordance with the invention is preferably from 40 to 85 percent

by weight of the dental filling material as inorganic and/or organic filler particles.

A dental filling material of the invention polymerizes to form epoxide-amine addition polymers within one or more of the general formulas I, II and III as follows:



wherein R is a moiety formed from a diepoxide;

R₁ is a substituted alkyl, having from 2 to 12 carbon atoms, cycloalkyl, substituted cycloalkyl, aryl having from 6 to 20 carbon atoms, substituted aryl, arylalkyl, or substituted arylalkyl,

R₂ is a difunctional alkyl, substituted alkyl having from 2 to 12 carbon atoms, cycloalkyl, substituted cycloalkyl, aryl having from 6 to 20 carbon atoms, substituted aryl, arylalkyl, substituted aryl, substituted arylalkyl,

and n, m, x and y each independently is an integer from 1 to 1,000. When substituted, R₁ and R₂ are independently substituted with one or more alkoxy, halogen, nitrate, acyl or carboxy alkyl moieties.

Diepoxides useful in dental filling compositions in accordance with the invention include diglycidyl ether of bisphenol-A (2,2-Bis[4-(2,3-epoxypropoxy)phenyl]propane), diglycidyl ether of bisphenol-F (is an isomeric mixture of Bis[4-(2,3-epoxypropoxy)phenyl]methane and the 2,4-homologous (CIBA-Geigy)), butanediol diglycidyl ether, N,N-diglycidylaniline, and Δ³-tetrahydrophthalic acid (sometimes referred to as bis(2,3-epoxypropoxy) cyclohex-3-ene dicarboxylic ester). Monoamines useful in accordance with the invention are aniline, p-flouraniline, benzylamine, 1-aminoadamantan, α-phenethylamine, dimethyl (aminomethyl) phosphine oxide and ethanolamine. Diamines useful in accordance with the invention are N,N'-dibenzylethylenediamine, N,N'-dibenzyl-3,6-dioxaoctandiamine-1,8,N,N'-dibenzyl-5-oxanonandiamine-1,9,N,N'-dibenzyl-(2,2,4)/(2,4,4) trimethylhexamethylenediamine.

Fillers useful in accordance with the invention are inorganic fillers including inorganic compounds, such as La₂O₃, ZrO₂, BiPO₄, CaWO₄, BaWO₄, SrF₂ and Bi₂O₃; organic fillers, such as polymer granulate; and combinations of organic and inorganic fillers.

Dental filling material in accordance with the invention overcomes the problems of prior art filling material, such as, discoloration and release of formaldehyde. Dental filling material in accordance with the invention provides the advantages of a low viscosity, relatively short setting time, relatively high solubility in organic solvents, thermoplastic behavior, and high radiopacity (RO) i.e., greater than 3 mm/mm Al. Higher

values of the radiopacity, for example radiopacity greater than 7, mm/mm Al are obtained using as fillers La_2O_3 , BiPO_4 , CaWO_4 and BaWO_4 .

For example a dental filling composition containing diglycidyl ether of bisphenol-A, N,N'-dibenzylethylenediamine and CaWO_4 show a viscosity (Brookfield) (η) of 2100 cP, a setting time of 3 hours and a radio-opacity (RO) of 9.2 mm/mmAl.

The invention provides dental filling material which is prepared from a two component paste system which is preferably introduced into roots using a lentulo or tubular needle because of the low viscosity. The dental filling material of the invention is formed with low shrinkage. This prevents contraction gaps and subsequent edge cracks of high shrinking materials. The dental filling material of the invention has low absorption of water and good adhesion to dentin. The composites formed therefrom are readily removable by heating, drilling or solublizing in organic solvents and are therefor useful as temporary filling materials.

The composition of the invention preferably has a viscosity of less than 20,000 centipoise and is preferably passed through a 1 mm diameter canal of a needle into a tooth root. The polymerizable epoxide monomer used in the composition of the invention preferably is a diglycidyl ether of bisphenol-A, diglycidyl ether of bisphenol-F, butanediol diglycidyl ether or Δ^3 -tetrahydrophthalic acid diglycidyl ester.

In Examples 1-4 setting times stated are determined in accordance with the method of ISO 6876 (1986-12-01: Dental root canal sealing materials).

Example 1

A dental filling material is obtained by mixing homogeneously 3.404 g (10.00 mmol) diglycidyl ether of bisphenol-A, (also referred to as 2,2 bis[4-(2,3-epoxypropoxy) phenyl] propane), 2.404 g (10.00 mmol) N,N'-dibenzylethylenediamine and 18.000 g CaWO_4 . This dental material has a viscosity (Brookfield) (η) of 3200 centipoise a setting time of 24 hours (at 37 ° C) and a radiopacity of 9.5 mm/mm Al. After the polymerization the dental filling product obtained is soluble in organic solvents such as CHCl_3 or CHCl_3 /ethanol-mixtures.

Example 2

Usable thermal setting dental filling composition is prepared as a two component paste system of part A and B.

Part A is obtained by mixing homogeneously 142.570 g (374.36 mmol) diglycidyl ether of bisphenol-A (also referred to as 2,2 bis[4-(2,3-epoxypropoxy) phenyl] propane), having a number average molecular weight (M_n) of about 380 g/mol, 11.680 g (37.44 mmol) diglycidyl ether of bisphenol-F (which is an isomeric mixture of bis[4-(2,3-epoxypropoxy)phenyl]methane and bis[2-(2,3-epoxypropoxy) phenyl] methane sold by CIBA-Geigy), and 241.463 g CaWO_4 , 60.366 g ZrO_2 , 0.637 g Fe_2O_3 and 4.277 g aerosil 200 (sold by Degussa).

The paste B is prepared by mixing homogeneously 22.064 g (205.90 mmol) benzylamine, 70.112 g (205.90 mmol) N,N'-dibenzyl-5-oxanonanediamine-1,9, 392.068 g CaWO_4 , 98.017 g ZrO_2 and 25.663 g Aerosil (sold by Degussa). The volume ratio of A mixed with B is 1:1. The setting time is 7 hours (at 37 ° C) and the working time 2:23 hours (at 23 ° C), respectively. The composition is characterised by the following values: radio-opacity (RO) of 11.6 mm/mm Al, flow 45 mm, film thickness 10 μm , solubility 0.23% (all according ISO 6876), and shrinkage 1.63 volume percent.

Example 3

Usable thermal setting dental filling composition is prepared as a two component paste system of part A and B.

Part A is obtained by mixing homogeneously 128.313 g (337.67 mmol) diglycidyl ether of bisphenol-A (also referred to as 2,2 bis[4-(2,3-epoxypropoxy) phenyl] propane) having a number average molecular weight (M_n) of about 380 g/mol, 10.535 g (33.77 mmol) diglycidyl ether of bisphenol-F (which is an isomeric mixture of bis[4-(2,3-epoxypropoxy) phenyl] methane, and bis[2-(2,3-epoxypropoxy) phenyl] methane sold by CIBA-Geigy), and 294.551 g CaWO_4 , 73.638 g ZrO_2 0.637 g Fe_2O_3 and 1.426 g Aerosil 200.

The paste B is prepared by mixing homogeneously 28.140 g (185.72 mmol) 1-amino-adamantane, 63.241 g (185.72 mmol) N,N'-dibenzyl-5-oxanonanediamine-1,9,8,554 g Aerosil 200, 365.519 g CaWO_4 , 91.380 g ZrO_2 and 11.364 g OL-31 (is a silicon oil sold by Bayer). The volume ratio of A mixed with B is 1:1. The setting time is 8 hours (at 37 ° C) and the working time is 16 hours at (23 ° C), respectively. The composition is characterised by following values: radio-opacity (RO) of 10.1 mm.mm Al, flow 35 mm, film thickness 15 μm , solubility 0.27 % (all according ISO 6876), and shrinkage 1.13 volume percent.

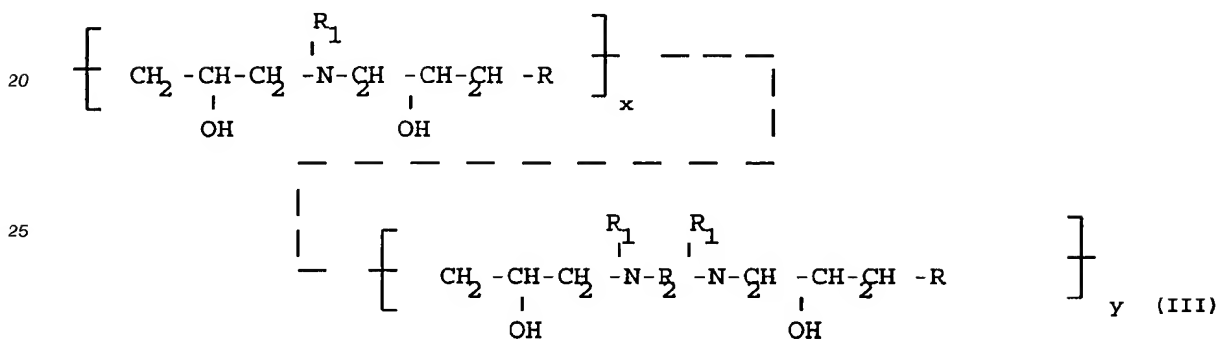
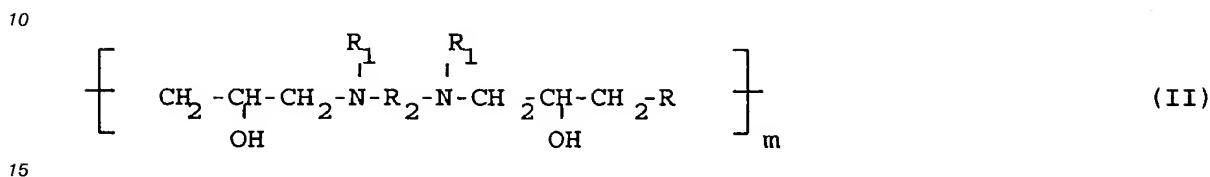
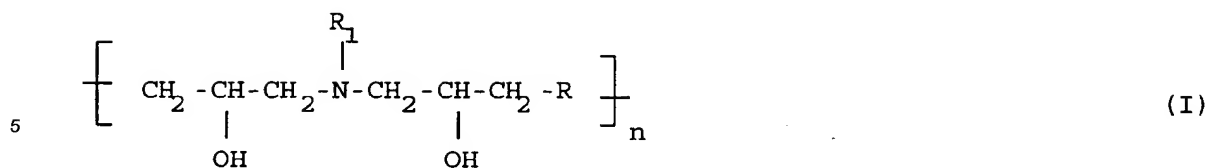
Example 4

A usable thermal setting dental filling material is obtained by mixing homogeneously 2.000 g (5.88 mmol) diglycidyl ether of bisphenol-A, 1.413 g (5.88 mmol) N,N'-dibenzylethylenediamine and 8.000 g La₂O₃. The setting time is 6 hours (at 37 °C) and the radio-opacity is 6.3 mm/mm Al.

It should be understood that while the present invention has been described in considerable detail with respect to certain specific embodiments thereof, it should not be considered limited to such embodiments but may be used in other ways without departure from the spirit of the invention and the scope of the appended claims.

Claims

1. A root canal sealing dental filling composition, comprising: liquid polymerizable organic monomers and filler, said polymerizable organic monomers comprising polymerizable epoxide moieties and an amine moiety, said epoxide monomer being a diepoxide, said amine containing monomer being a primary monoamine and/or a disecundary diamine, said filler comprising 40 to 85 percent by weight of said composition and providing a radiopacity of at least 3 mm/mm Al.
2. The composition of Claim 1 wherein said monomers polymerize to form a thermoplastic linear polymer adapted to seal a tooth root canal.
3. The composition of Claim 1 wherein said polymerizable epoxide monomer is diglycidyl ether of bisphenol-A, diglycidyl ether of bisphenol-F, butanediol diglycidyl ether or Δ^3 -tetrahydrophthalic acid diglycidyl ester.
4. The composition of Claim 1 wherein said monoamine is benzylamine, adamantanamine, α -phenethylamine or ethanolamine; said diamine is N,N'-dibenzylethylenediamine, N,N'-dibenzyl-3,6-dioxaoctandiamine-1,8,N,N'-dibenzyl-5-oxanonandiamine-1,9,N,N'-dibenzyl-(2,2,4)/(2,4,4)-trimethylhexamethylenediamine.
5. The composition of Claim 1 wherein said filler is La₂O₃, ZrO₂, BiPO₄, BaWO₄, SrF₂, Bi₂O₃ and/or polymer granules.
6. The composition of Claim 1 wherein said composition is formed from two-components which are adapted to be mixed together to initiate polymerization.
7. The composition of Claim 1 wherein said diepoxide, monoamine and/or diamine are adapted to form a composite which is soluble in CHCl₃, and/or C₂H₅OH.
8. The composition of Claim 1 wherein said filler provides a radiopacity of at least 3 mm/mm Al.
9. The composition of Claim 1 wherein said filler provides a radiopacity of at least 5 mm/mm Al.
10. The composition of Claim 1 wherein said composition is adapted to set at 37 °C within from 0.5 to 40 hours.
11. The composition of Claim 1 wherein said composition is adapted to set within from 0.5 to 3 hours.
12. The composition of Claim 1 wherein said composition has a viscosity of less than 5000 centipoise.
13. The composition of claim 1, wherein said amine monomer and said epoxide monomer are polymerized to form a polymer within the scope of at least one of general formulas:



wherein R is a moiety formed from a diepoxide;

R₁ is a substituted alkyl, having from 2 to 12 carbon atoms, cycloalkyl, substituted cycloalkyl, aryl having from 6 to 20 carbon atoms, substituted aryl, arylalkyl, or substituted arylalkyl,

R₂ is a difunctional alkyl, substituted alkyl having from 2 to 12 carbon atoms, cycloalkyl, substituted cycloalkyl, aryl having from 6 to 20 carbon atoms, substituted aryl, arylalkyl, or substituted arylalkyl, and n, m, x and y each index end entity is an integer from 1 to 1,000, and when substituted, R₁ and R₂ are independently substituted with one or more alkoxy, halogen, nitrate, acyl or carboxy alkyl moieties.

14. A method of sealing a tooth canal, comprising:

providing a canal in a tooth sealing said canal with a root canal sealing dental composition, comprising: liquid polymerizable organic monomers and filler said polymerizable organic monomers comprising an epoxide monomer and an amine monomer, said epoxide monomer being a diepoxide, said amine monomer being a primary monoamine and/or a dissecondary diamine, said filler comprising 40 to 85 percent by weight of said composition and providing a radiopacity of at least 3 mm/mm Al.

15. The method of Claim 14 wherein said polymerizable epoxide monomer is diglycidyl ether of bisphenol-A, diglycidyl ether of bisphenol-F, butanediol diglycidyl ether or Δ^3 -tetrahydrophthalic acid diglycidyl ester.

16. The method of Claim 14 wherein said monoamine is benzylamine, adamantanamine, α -phenethylamine or ethanolamine; said diamine is N,N'-dibenzylethylenediamine, N,N'-dibenzyl-3,6-dioxaoctandiamine-1,8,N,N'-dibenzyl-5-oxanonandiamine-1,9,N,N'-dibenzyl-(2,2,4)/(2,4,4)-trimethylhexamethylenediamine.

17. The method of Claim 14 wherein said filler is La₂O₃, ZrO₂, BiPO₄, BaWO₄, SrF₂, Bi₂O₃ and/or polymer granulate.

18. The method of Claim 14 wherein said composition is formed from two-components which are adapted to be mixed together to initiate polymerization.

19. The method of Claim 14 wherein said filler provides a radiopacity of at least 3 mm/mm Al.

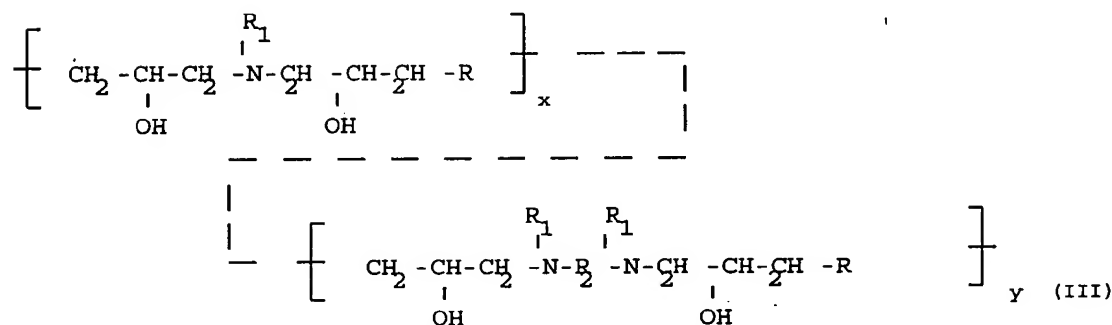
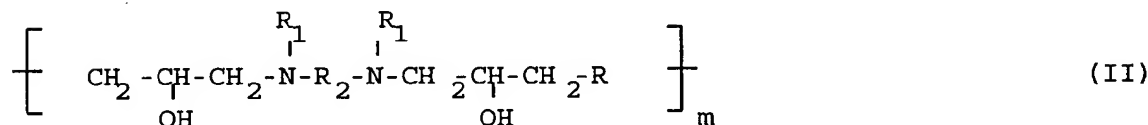
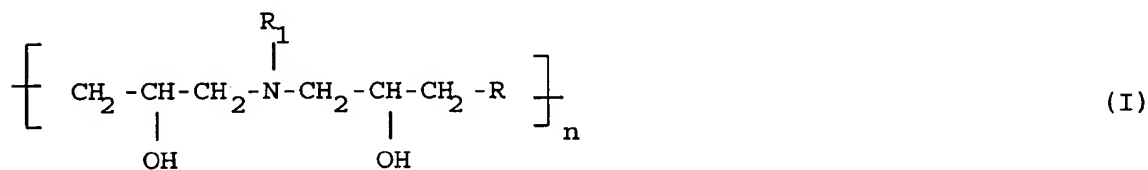
20. The method of Claim 14 wherein said composition is adapted to set within from 0.5 to 3 hours.

21. The method of Claim 14 wherein said composition has viscosity less than 20,000 centipoise and is passed through 1 mm diameter canal of a needle into a tooth root.

22. The method of Claim 21 wherein said composition polymerizes with less than 3% by volume shrinkage and has substantial adhesion to dentin.

23. The method of Claim 14 wherein said composition has a viscosity of less than 5,000 centipoise.

24. The method of claim 14 wherein said amine monomer and said epoxide monomer polymerize to form a polymer within the scope of at least one of general formulas:



wherein R is a moiety formed from a diepoxide;

R₁ is a substituted alkyl, having from 2 to 12 carbon atoms, cycloalkyl, substituted cycloalkyl, aryl having from 6 to 20 carbon atoms, substituted aryl, arylalkyl, or substituted arylalkyl,

R₂ is a difunctional monofunctional alkyl, substituted alkyl having from 2 to 12 carbon atoms, cycloalkyl, substituted cycloalkyl, aryl having from 6 to 20 carbonatoms, arylalkyl, or substituted arylalkyl,

and n, m, x and y each index end entity is an integer from 1 to 1,000, and when substituted, R₁ and R₂ are independently substituted with one or more alkoxy, halogen, nitrate, acyl or carboxy alkyl moieties.



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Application Number

which under Rule 45 of the European Patent Convention EP 95 10 4386
shall be considered, for the purposes of subsequent
proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	WO-A-93 10176 (ESSENTIAL DENTAL SYSTEMS) 27 May 1993 * page 6, paragraph 2 - page 7, paragraph 1 *	1,3-24	A61K6/00 A61K6/087
D	* page 3, paragraph 2 * & US-A-5 236 362 ---		
Y,D	GB-A-2 045 269 (ZEISS JENA VEB) 29 October 1980 * page 3, line 80 - line 107; claims; examples *	1,3,4, 6-16, 18-24	
Y	---		
Y	GB-A-2 199 839 (G C DENTAL IND CORP) 20 July 1988 * claim 4 *	5,8,9,17	
Y	---		
Y	DD-A-209 358 (FRIEDRICH SCHILLER UNIVERSITÄT) * page 1, paragraph 2; claims *	1,4	
A	---		
A	DD-A-244 748 (FRIEDRICH SCHILLER UNIVERSITÄT) * claims *	1,4	TECHNICAL FIELDS SEARCHED (Int.Cl.6) A61K
-/--			
INCOMPLETE SEARCH			
<p>The Search Division considers that the present European patent application does not comply with the provisions of the European Patent Convention to such an extent that it is not possible to carry out a meaningful search into the state of the art on the basis of some of the claims</p> <p>Claims searched completely : Claims searched incompletely : Claims not searched : Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search THE HAGUE		Date of completion of the search 6 July 1995	Examiner Cousins-Van Steen, G
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	EP-A-0 037 759 (COMMISSARIAT ENERGIE ATOMIQUE) 14 October 1981 * page 4, line 29 - page 6, line 14 * -----	1-24	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)



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-C-

Remark: Although claims 14-24
are directed to a method of
treatment of the human/animal
body (Art. 52(4) EPC) the search
has been carried out and based on
the alleged effects of the
compound/composition